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REACTIONS OF FREE RADICALS

Final report of Grant DA-ARO-D-31-124-G730,
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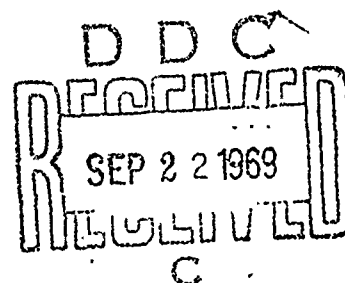
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Abstract

Results of research on the cleavage of triptycene and quinolizinium ions by alkali metals, and on the decomposition of substituted benzoyl peroxides and of cumyl peracetate are reported briefly.

The esr spectra of a series of triarylboron anion radicals show selective line broadening effects. The cleavage of triphenylboron by alkali metals in DME has been shown to give biphenyl in which both moieties of the biphenyl came from the same triphenylboron molecule. Several reactions of diarylboron derivatives with alkali metals are also discussed.

Part I. Publication List

J.E. Leffler, E. Dolan and T. Tanigaki, J. Am. Chem. Soc., 87, 927 (1965), "Aryl Boron Free Radicals"

M.M. Schwartz and J.E. Leffler, J. Am. Chem. Soc., 90, 1368 (1968), "Behavior of a Sigma Radical with a Peroxide Functional Group."

J.E. Leffler and H.H. Gibson, Jr., J. Am. Chem. Soc., 90, 4117 (1968), "The Radical-Induced Decomposition of Azides."

Part II. Participating Scientific Personnel

Dr. Teiichi Tanigaki

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Dr. E. Dolan

F.E. Scrivener (Candidate for Ph.D. 1969)

Dr. B.C. Menon

R.E. Schwerzel (Candidate for Ph.D.)

Dr. G. Watts

M.M. Schwartz (Received M.S. Dec. 1967, Candidate for Ph.D.)

D. Miller (Received M.S. 1969)

Part III. Unpublished Results

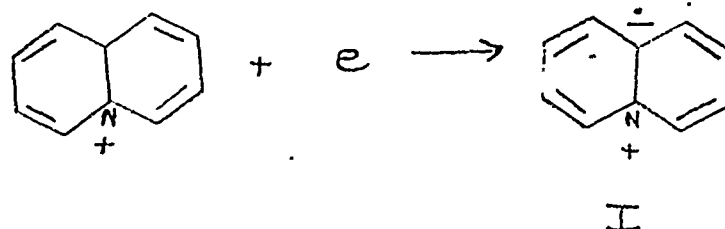
A. The Triptycene Anion Radical (B.C. Menon)

Attempted preparation of the triptycene anion radical from triptycene gave only 9-phenylanthracene, identified by its e.s.r. spectrum. This result will not be published in view of parallel work by T.D. Walsh and R.T. Ross, Tetrahedron Letters, 3123 (1968).

B. Radicals Derived from Quinolzinium and Related Compounds. (R.E. Schwerzel)

Attempted preparation of the radical I and related species with extended aromatic systems gave only broad esr signals or signals derived from cleavage products. This work may be submitted for

publication as a brief note concerning the direction of the cleavage reactions.



C. Photochemical Carboxy-Inversion Reactions (F.E. Scrivener)

Several unsymmetrically substituted benzoyl peroxides were photolyzed and found to give substantially complete radical rather than ion-pair reaction. See also C. Walling and M.J. Gibian, J. Am. Chem. Soc., 87, 3413 (1964).

D. Decomposition of Cumyl Peracetate (F.E. Scrivener)

This work, supported in part by ARO, will be presented for publication later this year after F.E.S. has put the finishing touches on his dissertation. Cumyl peracetate was shown to undergo ionic, free-radical and induced radical decomposition. The ionic decomposition is catalyzed by acids and by I_2 , which also acts as an inhibitor for the radical-induced decomposition.

E. Organoboron Radicals (G. Watts, Teiichi Tanigaki, E. Dolan, D.S. Miller)

Most triarylboron compounds react with alkali metals in DME to give anion-radicals with an e.s.r. spectrum showing a characteristic boron splitting and in most cases a resolved proton hyperfine splitting.

In the case of trimesitylboron anion radical in DME or liquid ammonia¹ the characteristic esr spectrum persists indefinitely, but for other compounds it is succeeded by the spectra of decomposition products, to be discussed in a later section.²

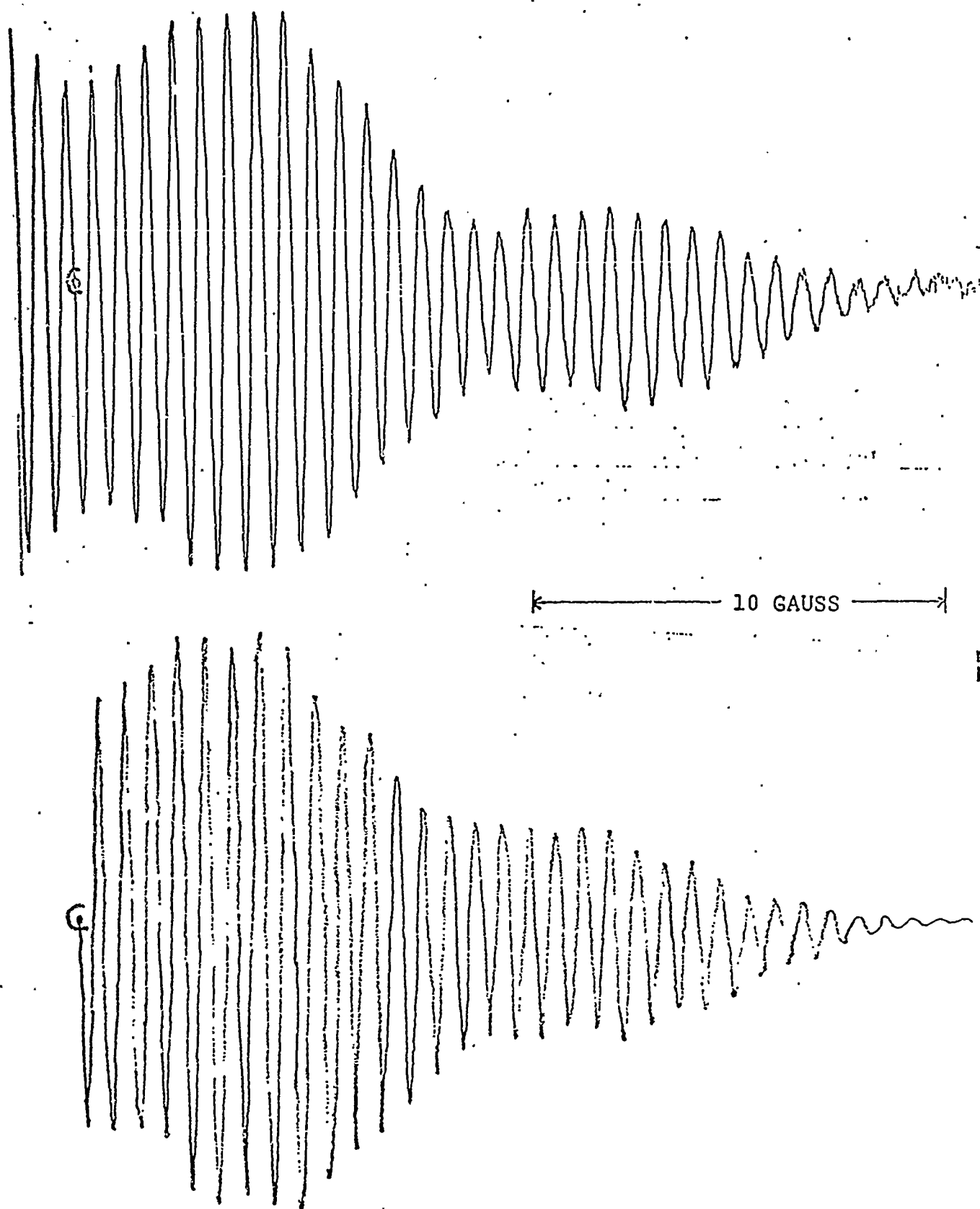


Figure 1. Top: ESR first derivative spectrum of ϕ_3B_2 generated from ϕ_3B and Li in DME. The use of Na/K alloy gives the same spectrum.

Bottom: calculated (first order) spectrum based on $a_B=7.84$, $a_{O-H}=1.99$, $a_{m-H}=0.675$, $a_{p-H}=2.70$ and using greater line-widths for the $\pm 3/2$ boron m_I values than for the $\pm 1/2$ boron m_I values.

Triphenylboron Anion Radical

The esr spectrum of triphenylboron anion radical consists of about 63 degenerate lines partly separated by the boron 3/2 spin into four groups. The splitting factors are $a_B = 7.86$ gauss, $a_{p-H} = 2.70$ gauss, $a_{O-H} = 1.99$ gauss, and $a_{M-H} = 0.675$ gauss. No gegenion splitting was detectable. The four main groups are the result of the splitting by the ^{10}B isotope of spin 3/2. The outer groups corresponding to $\tilde{m}_B = +3/2$ are only about 40% as intense as the $\tilde{m}_B = +1/2$ lines in the derivative spectrum as a consequence of selective line broadening. The high-field half of the spectrum is also slightly less intense than the low-field half; the $\tilde{m}_B = +1/2$ lines are about 85-90% as intense as the $\tilde{m}_B = -1/2$ lines, with a similar ratio for the $\tilde{m}_B = \pm 3/2$ lines.

The spectrum of trimesitylboron anion radical shows similar but much smaller line broadening effects; the $\tilde{m}_B = +3/2$ derivative amplitudes are about 70% of the $\tilde{m}_B = +1/2$ amplitudes. The $\tilde{m}_B = +1/2$ derivative amplitudes are equal within experimental error to those of the $\tilde{m}_B = -1/2$ lines. The hyperfine structure seems to be slightly more resolved on the high field side of the spectrum.

The assignment of splitting factors to the various ring positions and the validity of a model with three equivalent rings was tested by selective deuteration and computer plots³ of the spectra of both the perhydro and deuterated species. The deuterated species were tris(p-deuterophenyl)boron and tris(3,5-dideuterophenyl)boron and perdeutero-triphenylboron.

Fairly good fits to the experimental spectra were obtained using the boron and proton splitting constants cited above and the corresponding deuteron splitting constants. The variation in derivative amplitude between the $\widehat{m}_B = +1/2$ and $\widehat{m}_B = +3/2$ lines was duplicated by using linewidths of .346 and .410 gauss, respectively. A correction for the ^{10}B species was included, but the computer program used has no provision for second order shifts. The degree of fit presently attained is probably not yet optimized but is good enough to identify the splitting assignments beyond any doubt and to show that the three rings are equivalent or nearly equivalent on the esr time scale.

Dynamic Effects on the Triphenylboron Spectrum

The line-width variations in the triphenylboron spectrum contain information about the rate of motions of the radical or its individual phenyl groups. In principle, it should be possible to deduce the sign of a_B from the fact that the high-field lines are broader than those at low-field.⁴ In practice, this would require dubious assumptions about the anisotropy of the g-tensor and the influence of spin density on the adjacent carbon atoms.

In the case of the triphenylmethyl radical⁹ and the triphenylaminium ion-radical¹⁰ the necessary assumptions are more justifiable. The splitting factors obtained for triphenylmethyl by means of ENDOR⁵ and ESR^{5,6,7,8} are $a_{\text{O-H}} = 2.609$, $a_{\text{m-H}} = 1.143$ and $a_{\text{p-H}} = 2.857$ gauss⁵ and $a_{\text{OH}} = 2.53$, $a_{\text{m-H}} = 1.11$, $a_{\text{p-H}} = 2.77$, and $a_{\text{C}^{13}} = 26$ gauss.⁸ The high-field lines of the C^{13} triphenylmethyl spectrum are broader

than the low-field lines, indicating that the C^{13} splitting constant is positive.^{8,9}

The hyperfine constants for triphenylaminium cation radical¹⁰ are a_{O-H} 2.28, a_{m-H} 1.22, a_{p-H} 3.32, and $a_{N^{14}}$ 10.16. Again, the high-field lines are broader than the low-field lines and a_N is deduced to be positive.

The line width asymmetry between high and low fields in the spectra of the triphenylboron and related radicals is probably due to modulation of the anisotropic g tensor and electron-spin-nuclear spin dipolar interaction caused by Brownian motion.⁴ Although the assumptions about the g -tensor are less justified because planar aromatic hydrocarbon anion radicals may not be as good models for the triphenylboron radical as for the others, it is probable that a_B is positive in triphenylboron anion radical. On the other hand a_B in trimesityl boron is believed to be negative.¹ This difference may reflect the greater deviation from coplanarity in trimesitylboron.

The difference in line-width between the $\tilde{m}_B = +1/2$ and $\tilde{m}_B = +3/2$ lines could be the result either of the Brownian motion of the molecule or of some process that modulates the hyperfine constants, for example a libration of the rings or a motion of solvent molecules or gegenions. While we are unable to identify this process completely, the fact that the effect is smaller in trimesitylboron anion radical even though a_B is greater (10.2 gauss) suggests that it is not Brownian motion. An attempt to improve resolution by either raising or lowering the temperature showed that the best resolution was obtained near room temperature. This suggests

modulation due to variable solvation superimposed on that due to Brownian motion: the contribution due to Brownian motion should decrease at higher temperatures while a solvation effect might well behave in the opposite way.

Other Tri-substituted Boron ESR Spectra

We have also briefly examined the esr spectra from the reaction of several other triarylborons with alkali metals in DME.

Tris-p(tolyl)boron gave a spectrum resembling that of triphenylboron, but no detailed analysis was made. Tris-(2,4,6-trimethyl-3,5-dinitrophenyl)boron¹¹ gave an initial spectrum consisting of three broad lines, 1:2.5:1 with a 20 gauss splitting; this was succeeded by the spectrum of dinitromesitylene anion radical.¹² Tris-(p-dimethylaminophenyl)boron^{13,14} gave a spectrum consisting of four broad lines with further incompletely resolved fine structure and a main 8.2 gauss spacing attributable to the boron anion radical; the signal changed on standing and will be discussed further in a later section.

Tris-(p-chlorophenyl)boron gave a signal completely identical to that from unsubstituted triphenylboron. This surprising result means that the replacement of chlorine atoms by hydrogen is much faster than the cleavage of the triarylboron. The final spectrum was that of diphenyl anion radical, the main cleavage product of triphenylboron. However, p,p'-dichlorobiphenyl is rapidly reduced to biphenyl under the same conditions.¹⁷

Tris-(p-methoxyphenyl)boron^{14,15} also gave a four line ¹¹B signal of about 8.1 gauss splitting. It had some partly resolved proton fine structure, more nearly resolved in the $\tilde{m}_B = \pm 1/2$ groups than in the $\tilde{m}_B = \pm 3/2$ groups.

Triethylboron and tri-n-propylboron failed to give ESR signals on treatment with Na/K in DME, although the metal was consumed. Tribenzylboron¹⁵ reacted with Na/K in DME to give a dark green solution whose esr signal consisted of a single broad line extending over about 30 gauss. Tris(cyclohexyl)boron gave only a very weak and unstable signal.

Reductive Cleavage of Triarylborons

The reaction of triarylborons with alkali metals gives an anion radical which is stable indefinitely in some cases,¹ but which in other cases is subject to a cleavage reaction (1) of unknown mechanism.^{1,2} An alternative reaction (2) has been observed only in the case of triphenylboron and tris-(p-tolyl)boron.



The stable anion radicals are those that are both sterically hindered and without strongly electron-attracting substituents. For example, the anion radical from trimesitylboron is stable, contrary

to our earlier report.^{2,16} On the other hand we find that tris-(2,4,6-trimethyl-3,5-dinitrophenyl)boron cleaves rapidly to give the well-known esr signal of the dinitromesitylene anion radical,¹² and the less hindered tris(2,4-dimethylphenyl)boron cleaves to give unknown products but probably also by a type -1 reaction.¹⁰

Compounds known to cleave by reaction (1) are tris(o-xenyl)-boron,^{1a} and tris(α -naphthyl)boron.^{1a}

Tris-(p-dimethylaminophenyl)boron certainly does not cleave by reaction (2) or the esr of the biphenyl would have been detected on further exposure to the metal; possibly it cleaves according to reaction (1) which would give a product that would not give an esr signal with alkali metal at room temperature in DME. Reaction (1) should be accompanied by the formation of some other boron species. On further treatment of tris(p-dimethylaminophenyl)boron with Na/K in DME the original 4-line signal, $a_B = 8.3$ gauss, is replaced by a signal consisting of seven broad lines of relative intensities 1:2:3:4:3:2:1 at intervals of 3.1 gauss; it regenerates the original four-line signal on standing. This is definitely not a biphenyl anion signal. A species with strong interactions from two equivalent boron nuclei might be expected to give a seven-line signal with these relative intensities.

The reaction of tris(p-methoxyphenyl)boron¹⁴ with Li in DME gives a four line signal that decays on further reaction to a weaker and narrower signal. It does not give the easily detected biphenyl anion radical signal, even though control experiments with p,p'-dimethoxybiphenyl show that this substance is reduced to biphenyl under

our conditions.¹⁷ It has further been shown that anisole also gives biphenyl anion radical on reaction with Li in DME. Hence both reactions (1) and (2) are excluded for this triarylboron. Prolonged reaction gave a precipitate that was not further investigated.

The Triphenylboron Cleavage Reaction

The reaction of triphenylboron with alkali metals in DME first gives the esr signal of the triphenylboron anion radical and then that of the biphenyl anion radical. Since the methods of synthesis of the borane via Grignard reactions give biphenyl as a side product, we tested our triphenylboron for this impurity by thin-layer chromatography and by H₂O₂ oxidation of the triphenylboron followed by an alkali metal esr test for biphenyl. These tests, the latter one very sensitive, failed to show any biphenyl impurity in our triphenylboron. The oxidation was necessary because triphenylboron in DME has a greater electron affinity than biphenyl and esr signal from triphenylboron containing a small amount of added biphenyl is just that of the triphenylboron anion radical.

Cleavage by reaction (1), leading to benzene, is a very minor process. Benzene was shown to be a product by examining the u.v. spectrum of the distillate from the cleavage reaction. However, the yield of benzene as determined by vapor phase chromatography and spectroscopy is less than 2%. The boron-containing products of the cleavage reaction are presumed to be derivatives of phenylboronic acid.^a The possibility of intermediates containing two boron atoms

^a A nearly quantitative yield of phenylboronic anhydride was obtained from an experiment with diphenylboron chloride and Na/K in DME. Diphenylboron chloride in DME disproportionates and gives the ϕ_3B^- esr signal followed by a ϕ_2B^- esr signal.

will be discussed in a later section.

The biphenyls formed by the reaction of tris-(p-tolyl)boron or deuterium-labeled triphenylboron are bonded at the same carbon that was initially bonded to boron. Thus the product from tris-(p-tolyl)boron is p,p'-dimethylbiphenyl, and that from tris-(p-deuterophenyl)boron is p,p'-dideuterobiphenyl. More significant is the fact that the reaction is entirely intramolecular, both moieties of the biphenyl having come from the same triphenylboron molecule. This was demonstrated by an experiment in which a mixture of equal amounts of tris-(p-deuterophenyl)boron and tris-(3,5-dideuterophenyl)boron was treated with Li in DME. The signal from the mixture of triarylboron anion radicals was succeeded by an esr signal from a mixture of deuterated biphenyls. The esr spectrum matches that plotted by the computer for an equal mixture of the two symmetrical biphenyls using experimentally determined splitting constants. This is a good test for the absence of unsymmetrical biphenyl because that species should have a peak in a region where there is no interference from the two symmetrical biphenyls.

There are two precedents for the intramolecular formation of biaryls from arylboron compounds. One is the formation of di- α -naphthyl in good yield from the photolysis of tris(α -naphthyl)boron in CCl_4 .¹⁸ Experiments with bis-(α -naphthoyl) peroxide have shown that free α -naphthyl radicals are almost entirely converted to α -chloronaphthalene, and hence can not be intermediates in the formation of binaphthyl. The other example is the exclusive formation of symmetrical biphenyl by the electrode oxidation of a mixture of

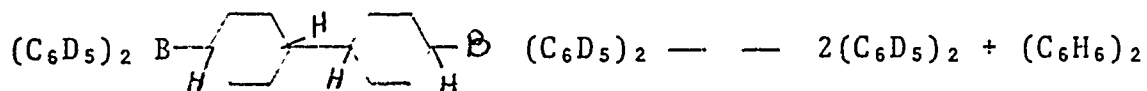
labeled and unlabeled tetraphenylborate ion, with benzene as a byproduct.¹⁹

Biphenyl has also been observed as a product of the reduction of triphenylamine,²⁰ and triphenylphosphine,²¹ and in the mass spectra of triarylcarbinols.²² Substituent effects in the latter reaction suggested an attack by a radical site on one aryl group on the polarizable π electrons of the other aryl group, with elimination of the bridging moiety.

Possible Diboron Compounds. — The reaction of tris-(p-dimethylaminophenyl)boron with Li in DME gave only the four-line boron radical signal, $a_B = 8.3$ gauss, with no resolved proton or nitrogen hyperfine structure. This signal gradually decayed on prolonged reaction with Li. A similar experiment with Na/K, however, gave different results: After about fifteen minutes the four-line boron signal was succeeded by a seven line signal, 1:2:3:4:3:2:1 relative intensities, with a 3.1 gauss interval. This is the spectrum to be expected if the signal is split by two equivalent boron atoms.

A partly resolved signal with seven lines at about 2.8 gauss intervals was obtained by treating perdeutero diphenylboron chloride with alkali metal in DME. A better signal with seven lines matching the expected intensities for the two-boron model (including a B^{10} correction) was obtained by carrying out the initial reaction in benzene at room temperature, then changing the solvent to DME. The interval between the lines in this signal was 2.93 gauss.

Further reaction of this material with sodium-potassium alloy and DME caused the disappearance of the seven-line signal and its replacement by a four-line signal very much like that obtained from the reaction of perdeutero triphenylboron, $a_B = 8.3$ gauss, and no additional hyperfine structure. Still further exposure to alkali metal produced a signal attributable to a mixture of biphenyl and perdeutero biphenyl. This signal was reproduced precisely by computer simulation assuming a biphenyl perdeutero biphenyl ratio of 0.5 and including none of the unsymmetrical pentadeutero biphenyl. It should be noted that the unsymmetrical pentadeutero biphenyl would have been readily detected. This result shows that diphenylboron chloride does not form a radical that attacks benzene to give triphenylboron, since this would have given some of the unsymmetrical biphenyl. To explain the 2:1 ratio of products, it is necessary to assume that each $(C_6D_5)_2BCl$ gives rise to $1/2$ of a biphenyl precursor. A further restriction is that the presumed two-boron species must not contain any protons in positions that would give rise to large proton coupling constants. This rules out structures such as I for the species with the 7-line signal.



I

However, it is necessary for the intermediate formed during the reaction in benzene to incorporate benzene in some way before the

solvent is replaced by DME. .

In a search for boron compounds incorporating benzene we carried out the room-temperature reaction of diphenylboron chloride with Na/K in benzene for longer reaction times and without replacing the solvent with DME. A two-day reaction period gave a small amount of diphenylboronic acid in work-up. Longer reaction times gave a pyrophoric black precipitate containing all of the boron, leaving no boron compounds in the benzene. The reaction of diphenylboron chloride with Na/K in cyclohexane also gave a black pyrophoric precipitate. The solvent contained a compound with uv, nmr, and ir spectra resembling those of triphenylboron, but a pure sample was not obtained. Somewhat similar experiments by Auten and Kraus²³ with di-n-butylboron chloride and potassium in ether gave tributylboron and potassium di-n-butylboride. Kuchen and Brinkmann²⁴ obtained a pyrophoric solid of composition (C_6H_5B) by heating phenylboron dichloride.

One rationalization of the reaction of perdeutero diphenylboron chloride with Na/K in benzene, then in DME, is that the benzene stage of the reaction produces a $(C_6D_5)_2BM$ -benzene adduct which on transfer to DME and further reaction gives $(C_6H_5)_2$ plus $(C_6D_5)_2\overset{\cdot}{B}-B(C_6D_5)_2$, responsible for the seven-line signal. Further reduction of this diboron species in DME then gives $(C_6D_5)_2\overset{\cdot}{B}:OR_2$, for the renewed four-line signal, and finally $(C_6D_5)_2$.

Attempts to stabilize boron radical intermediates as perdeutero-pyridine or pyridine adducts as reported by Köster²⁵ gave only γ -dipyridyl esr signals.

Disproportionation Reactions of Arylboron Compounds

Treatment of compounds of the type Ar_2BX with alkali metals in DME gives the esr spectrum of the corresponding $\text{Ar}_3\text{B}^\cdot$; this is usually the first resolved signal seen, except in the case of diphenylboron chloride which gave a seven-line signal first. Examples are diphenylboron chloride, dimesitylboron fluoride,¹⁶ and diphenylboronic anhydride.

The signals from phenylboronic anhydride and phenylboron dichloride were unresolved.

The work on organo-boron chemistry is being prepared for publication in a journal.

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<p>Results of research on the cleavage of triptycene and quinolizinium ions by alkali metals, and on the decomposition of substituted benzoyl peroxides and of cumyl peracetate are reported briefly. The esr spectra of a series of triarylboron anion radicals show selective line broadening effects. The cleavage of triphenylboron by alkali metals in DME has been shown to give biphenyl in boron molecule. Several reactions of diarylboron derivatives with alkali metals are also discussed.</p> <p><i>of a series of triarylboron anion radicals, the esr spectra show selective line broadening effects. The cleavage of triphenylboron by alkali metals in DME has been shown to give biphenyl in boron molecule. Several reactions of diarylboron derivatives with alkali metals are also discussed.</i></p>			
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